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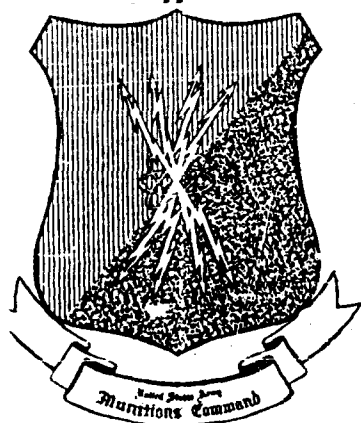
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DIFFERENTIAL THERMAL ANALYSIS
OF POTASSIUM PERCHLORATE

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by

**David A. Anderson
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March 1963

**Feltman Research Laboratories
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ABSTRACT

Differential thermal analysis and thermogravimetric analysis experiments were carried out on potassium perchlorate. The thermograms clarify conflicting reports in the literature concerning details of decomposition and elucidate the thermodynamics of this reaction.

DISCUSSION

In a paper by Gordon and Campbell published in 1955 (Ref 1), the differential thermal analysis of potassium perchlorate is illustrated from the point of view of the characterization of this compound rather than the details of its decomposition. In this work, for which the differential thermal analysis was carried out in a test tube in an open furnace, a large endotherm following the initial exotherm after fusion was observed. Later, Markowitz and Boryta (Ref 2) became interested in the details of decomposition as revealed by differential thermal analysis and pointed out that this endotherm is due to the molten sample rising up the sides of the tube resulting in separation of the sample from the thermocouple. This gives rise to an apparent endotherm at that point. These authors attempted to overcome the thermal effects which accompany the separation of the sample from the thermocouple by carrying out the thermal analysis in a closed furnace system. Although the endotherm in question is not observed under these conditions, the details of the decomposition are missed, undoubtedly because a large mass of sample was used in these experiments and heat transfer conditions in the closed furnace system were poor.

The approach in conducting the differential thermal analysis experiments in the present work is to adjust the mass of the sample and the dimensions of the sample container so that the decomposing gases will not force the reacting mass up the tube. Thus, intimate contact of the sample with the thermocouple is maintained throughout the entire reaction, which is, after all, the best condition for the differential thermal analysis experiment. It was found that when 500 mg or less of potassium perchlorate is contained in a test tube with an inside diameter of 16 mm, separation of the sample from the thermocouple does not occur. These experiments show that it is possible to obtain detailed differential thermal analysis curves for decomposition reactions which are accompanied by violent foaming and bubbling by adjusting sample weight and geometric parameters. In this work, the detailed differential thermal analysis curve for the decomposition of KClO_4 is presented for the first time.

It reveals two exothermal processes, one occurring during decomposition prior to the precipitation of KCl and the other occurring simultaneously with the precipitation of KCl . This was determined in differential thermal analysis experiments carried out in a metal block in which provision was made for observing the sample as it was heated (Ref 1).

Figure 1 shows curves for both differential thermal analysis and thermogravimetric analysis carried out simultaneously on an 86-mg sample of KClO_4 . The sample mass used in these experiments is less than 1/50 as great as that used by the referenced authors. The differential thermal analysis curve is essentially identical to the dta curves obtained with 500-mg samples using the furnace block. It shows an endotherm due to melting with a peak at approximately 606° . After the sample melts, the reaction becomes exothermal. The exothermicity decreases as the temperature approaches approximately 638° . At 638° , a sharp rise in exothermicity occurs, with a peak at 641° followed by the rapid decay of the exotherm.

The thermogravimetric analysis curve shows that weight loss due to decomposition occurs simultaneously with the endotherm for melting and is complete at the peak of the final exotherm. This curve shows a single, smooth, sigmoidal-shaped weight loss curve with no inflections corresponding to the thermal changes which occur during the reaction. Decomposition occurs throughout melting as well as in the exothermal regions of reaction. Before the final exothermal band was reached at 638° , the sample underwent 67% decomposition. Observations made in separate experiments show that, after melting and during the first exothermal step of decomposition following melting, the decomposing mass is clear. The final exothermal band is observed to occur during the precipitation of potassium chloride.

Since the net decomposition of KClO_4 to form chloride liquid and oxygen is reported to be endothermal (Ref 2), the fact that an exothermal reaction occurs prior to 638° in the clear molten mass remains to be explained. This is not easy since, in spite of the fact that the decomposition of KClO_4 has been studied, the mechanism of reaction is not well understood (Refs 3, 4, 5). It was found from additional differential thermal analysis experiments that, from the peak of the endotherm to the end of the first exothermal side band at approximately 638°C , the ClO_3^- ion concentration is relatively constant compared to the formation of Cl^- ion. The ClO_3^- ion concentration decreased from approximately 19% to 12% and the Cl^- ion concentration increased from 2% to 24%. The overall reaction since the ClO_3^- ion is present in an approximately steady state concentration, is:



The most reasonable explanation for the exothermal side band from 606° to 638° is that the liquid state reaction is exothermal, contrary to previously reported conclusions (Refs 2, 6) concerning this liquid state decomposition reaction. Thermodynamic calculations at 618° show that, unless the existing heat of formation, heat of transition, and heat capacity values are grossly incorrect, this reaction should be exothermal by approximately -8 Kcal/mole. The values used for this determination are ΔH_f (KCl)⁷ solid at 25° C = -104.2 Kcal/mol, ΔH_f ⁷ (KClO₄) solid at 25° C = -103.6, specific heat at 100° C for KCl⁸ = 0.17 cal/g° C, specific heat for KClO₄⁸ at 30° C = 0.9 cal/g° C, ΔH for crystalline transition + fusion⁶ for KClO₄ = 5.5 Kcal/mole, ΔH ⁸ fusion (KCl) = 5.5 Kcal/mole. In these calculations, the heat capacity was taken as constant up to 618°C since data on the change in heat capacity as a function of temperature was not available for KClO₄. However, this should not alter the results appreciably, or change the conclusions.

EXPERIMENTAL PROCEDURE

Two series of differential thermal analysis experiments were conducted. In the first series, the apparatus, which is described in Reference 1, consisted of a metal block in which test tubes containing the samples and reference materials were located. The metal block was heated at a rate of 10° C per minute, and the differential temperature vs sample temperature was recorded on a Moseley Autograph, Model 3 X-Y recorder. A West Gardsman proportioning controlled was used to monitor the rate of heating. In these experiments, bare 28-gage chromel-alumel thermocouples were located in the sample and in the reference material. The sample weight was approximately 500 mg and, in both series of experiments, doubly recrystallized Fisher scientific reagent grade KClO₄ was used.

The second series of experiments involved obtaining both the differential thermal analysis and the thermogravimetric analysis curves simultaneously on about 86 mg of KClO₄. The apparatus used consisted of an analytical balance which was adapted for automatic recording by means of a linear differential transformer. A rod supported on one end of the balance beam and standing in a vertical position above the balance was used to support the sample and reference materials which were contained in 16 mm test tubes approximately 1 1/2 inches long. The sample and reference materials were mounted one above the other. Chromel-alumel, 38-gage thermocouples were placed in both the sample and reference compounds. The furnace was lowered over the test tubes. Weight changes

and differential temperature were simultaneously recorded in a Brown strip chart recorder. The heating rate was programmed at 10° C per minute. In all cases, replicate experiments were conducted. The chloride was determined gravimetrically by precipitation with a standard silver nitrate solution. The chlorate was first reduced to chloride by formaldehyde and the solution was then treated with silver nitrate. The perchlorate was calculated by difference.

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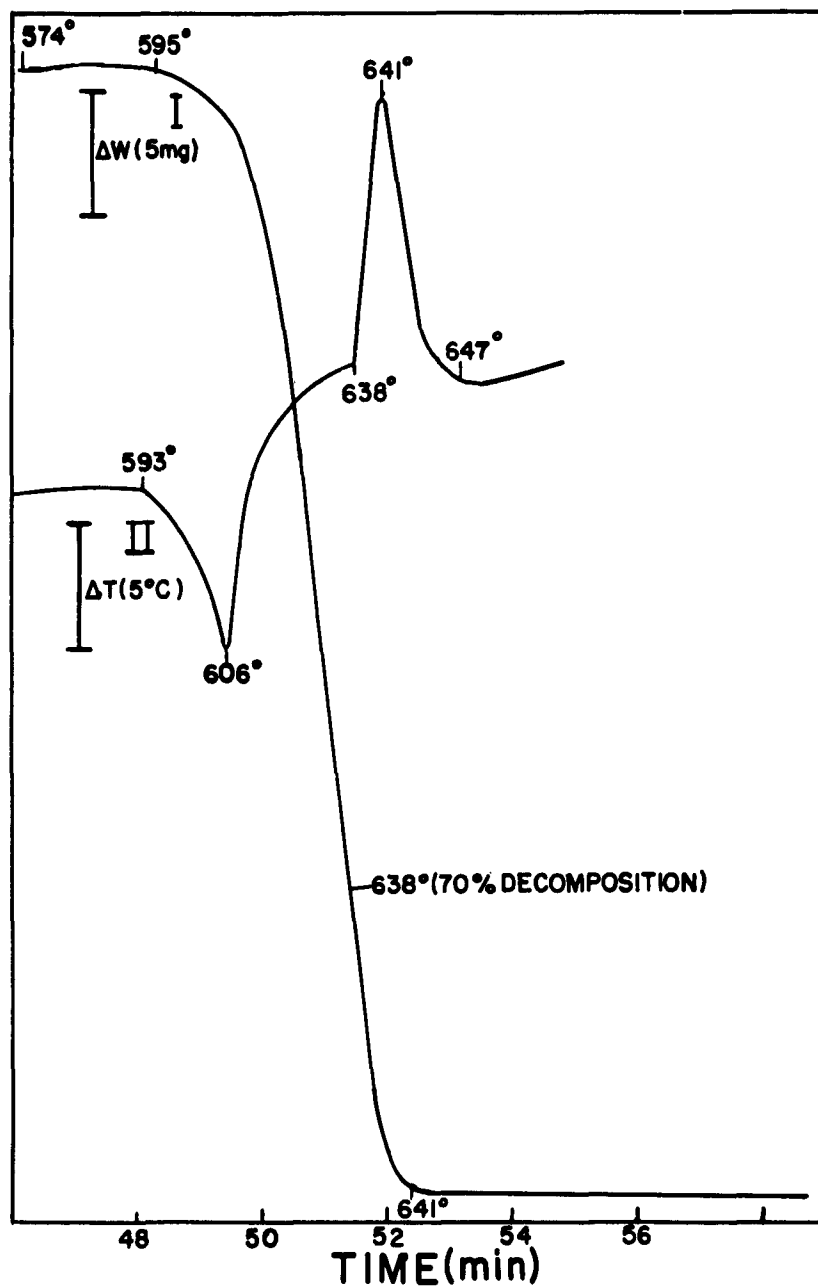


Fig 1 Simultaneous thermogravimetric analysis (I) and differential thermal analysis (II) curves for an 86-mg sample of $KClO_4$ heated in air at a rate of $10^\circ C/min$

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